

The Origin of Persistent Photoconductivity in Hydrogenated Amorphous Silicon

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The origin of the persistent photoconductivity (PPC) in hydrogenated amorphous silicon, specifically doping-modulated npnp ... type superlattices and unlayered, compensated films has been reexamined. Previous models with AX centers, dangling bonds and P-B complexes as well as very recent proposals by Kakalios and by Fritzsche et al. are compared with respect to our very recent experimental results. The result of analyses lead to the conclusion that hole induced dopant conversion and following dangling bond formation processes are responsible for PPC in both doping-modulated superlattices and compensated films.

I. INTRODUCTION

The persistent photoconductivity (PPC) is a light-induced excess conductivity persisting long after the termination of illumination and has been observed in heterostructures and superlattices.¹⁻²⁸ The first observation of PPC in superlattices was made by Dohler⁶ in 1982 in nipi... type doping-modulated GaAs superlattices at low temperatures below 80 K and he showed that the charge separation by the modulation field was the origin of PPC at low temperatures.²⁹⁻³¹

In the case of amorphous semiconductors, the first observations of PPC were made by Aker and Fritzsche⁷ and author's group⁸ in unlayered, boron-doped hydrogenated amorphous silicon (a-Si:H) in 1983, and by Mell and Beyer⁹ also in unlayered but compensated a-Si:H films in the same year all at room temperatures. In 1984, Hundhausen and Ley¹⁰ observed PPC in nipi... type doping modulated a-Si:H superlattices at low temperatures, while Kakalios and Fritzsche¹¹ reported very large PPC in npnp ... type superlattices at room temperature.

Since the charges separated by modulation field would recombine quickly over the potential barriers at room temperature, those large PPC observed at room temperature was hard to understand. Thus many different models were proposed in the past decade but the exact mechanism of PPC is still in controversy. In this paper existing models are reviewed and, based on new experimental results, a new comprehensive model which can explain PPC

in doping-modulated superlattices as well as in unlayered compensated a-Si:H films, will be presented.

II. EXPERIMENTALS

Doping-modulated a-Si:H npnp ... superlattices were prepared by glow discharge decomposition of alternation gas mixtures of silane (SiH_4) plus phosphine (PH_3) and silane plus diborane (B_2H_6) at substrate temperature of 250°C . Gas phase doping concentrations of dopants were 200 ppm or 500 ppm both for n- and -players. Thickness of each layer was either 360 Å or 400 Å. For coplanar conductance measurements the multilayer films were scratched with a diamond scribe before deposition of Al electrodes in order to assure contacts to all individual layers. For the transverse conductance measurements, Cr electrodes were coated on the top n-layer of the superlattice films deposited on tin oxide coated glass.

Compensated films were produced by glow discharge decomposition of the mixture of silane with phosphine and diborane, 500 ppm each. The conventional coplanar samples and Schottky barrier type samples were prepared. The Schottky barrier (SB) sample structure was TCO/n⁺/compensated a-Si:H/Pd of about $1\mu\text{m}$ in thickness. Before conductivity measurement, the samples were annealed at 180°C for 30 min. in a vacuum of 10^{-6} torr to remove the effect of prior light exposure.

III. RESULTS

Figure 1 shows the illumination-time dependence of PPC in a npnp ... type doping-modulated superlattice doped with 200 ppm P or B each layer. As seen in the figure, PPC

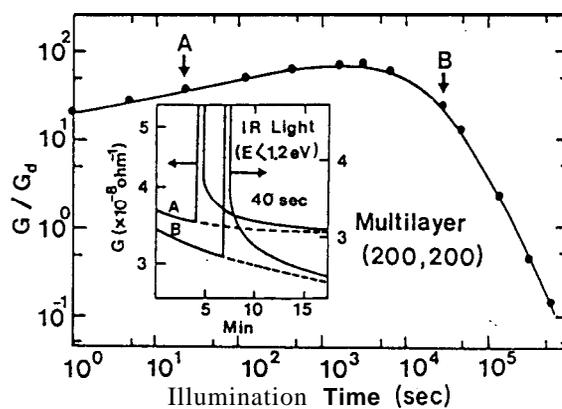


FIG. 1. Illumination-time dependence of PPC (G/G_d) in a npnp... doping-modulated superlattice doped with 200 ppm of P or B in each n- or p-layer. G is the conductance measured 4 mm after the termination of band-gap light illumination at 100 mW/cm^2 and G_d is the dark conductance at annealed state. Inset shows the effect of IR light ($h\nu < 1.2\text{eV}$, 40 sec) illumination at A and B. [After Ref. 25]

increases with illumination time upto 1000 sec, then levels off and start to decrease, and finally goes down even below the annealed-state value ($G/G_d = 1$) at about 10^5 sec. The decrease is due to the defect formation near midgap.²⁷ This means that the PPC effect and defect formation by illumination compete each other with PPC effect saturation faster.

Figure 2 depicts the annealing temperature dependence of PPC for the multilayers with n-channel conduction composed of 200 ppm doped layers for both n- and p-layers (200, 200), and with p-channel conduction composed of 2 ppm n-layers and 1000 ppm p-layers (2, 1000). The p-channel sample anneals out below 100°C , while the n-channel superlattice even decreases further before the defects anneal out at about 160°C . The PPC

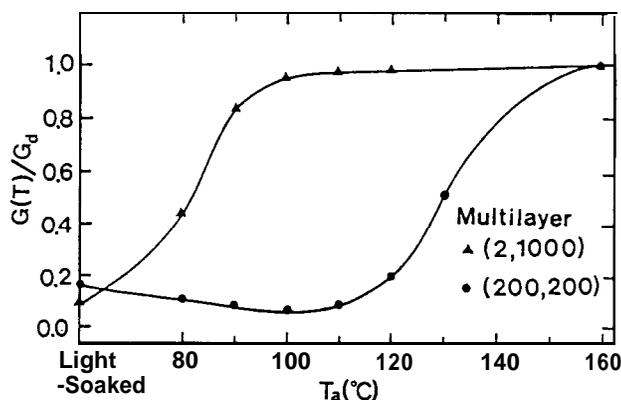


FIG. 2. Annealing temperature dependence of PPC (G/G_d) for the superlattice with n-channel conduction having n- and p-layers both doped with 200 ppm (\bullet), and for the superlattice with p-channel conduction composed of 2 ppm P doped n-layers and 1000 ppm B doped p-layers (Δ). Annealing time was 30 min at each temperature. [After Ref. 25]

anneals out at lower temperatures than dangling bonds. If PPC anneals out at lower temperatures than defects. Those light-induced defects are well established as dangling bonds. It is also well known facts that dangling bonds anneal out at about 100°C in p-layers and at about 160°C in n-layers. Thus dangling bonds can be formed both in n- and p-layers after prolonged illumination.

Figure 3 is the plot of dark conductance vs inverse temperature. Dotted line represents conductance curve after 30 min. illumination (PPC state) and dot-dashed curve is after 2 days of light-soaking (Staebler-Wronski state) for the (200, 200) multilayers, while the solid line represents the annealed state. As one can see from the curves in the figure, PPC definitely anneals at lower temperature than dangling bonds in n-layers.

Figure 4 shows current density vs voltage (J-V) characteristics of the compensated, unlayered film of Schottky barrier (SB) structure after the illumination of band gap light with 1 mW/cm^2 . Solid lines represent annealed state, forward and reverse bias curves. After 1 hour illumination both the forward and reverse currents increased considerably. These changes can be reversed by annealing. Since the built-in voltage in this SB structure is less than 1V, the forward current at above 1V may be thought of being due to the bulk conductance due to PPC effect. The increase of reverse currents should be due to the increase

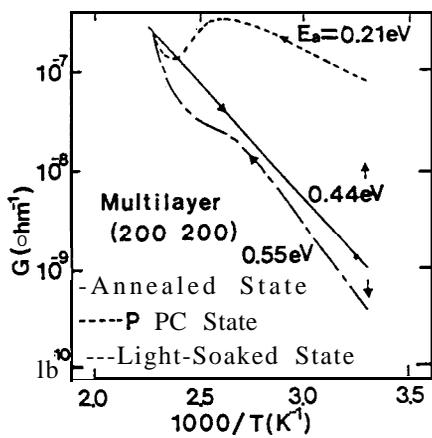


FIG. 3. Temperature dependence of dark conductance after 30 min (PPC state) and 2 days (Staebler-Wronski state) of illumination at 100 mW/cm^2 at room temperature for the superlattice composed of n- and p-layers both doped with 200 ppm. [After Ref. 25.]

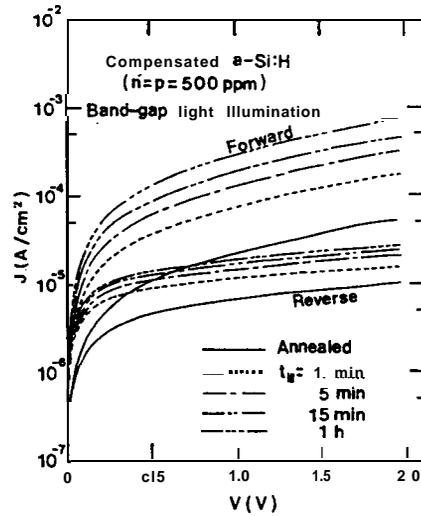


FIG. 4. Current density vs voltage characteristics of the compensated, unlayered film of Schottky barrier structure after the illumination of band gap light of 1 mW/cm^2 intensity through the Schottky barrier side. Band gap light used was of filtered wavelength between 6000 Å and 8000 Å [After Ref. 39]

in defect density in the Schottky barrier region near Pd electrode, judging from the results of our recent works on bias-induced metastable changes.^{32,33}

Figure 5 shows dark J-V characteristics of compensated SB structure film after hole injection from the TCO side by blue light illumination at 1 mW/cm^2 . After hole injection, the increase in forward currents is as large as the case of band gap light illumination. Since

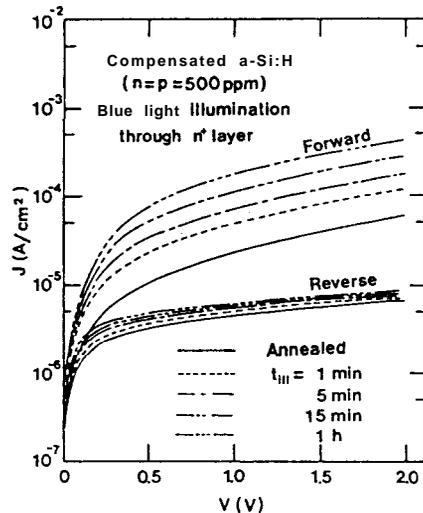


FIG. 5. Dark current-voltage characteristics of compensated Schottky barrier structure film after hole injection from the TCO side by blue light illumination at 1 mW/cm^2 . Wavelengths of blue light ranges between 3000 Å and 5000 Å. [After Ref. 39]

the absorption depth of the blue light is less than 1000 \AA , most electron-hole pairs are generated near n^+ (TCO) region and only holes pass through the bulk of the compensated film. On the other hand the reverse currents are remain practically unchanged after hole injection. This implies that the hole injection is less efficient in creating defects in SB region than band-gap light illumination.

Figure 6 shows the J-V characteristics of SB structure after electron injection by the illumination of blue light at 1 mW/cm^2 from the Schottky barrier side. In this case the forward currents increased little while reverse currents increased even more than the case of band-gap illumination (Fig. 5). Thus defect creation at SB region is due to the electron injection while PPC is enhanced by the hole injection. This is an important result: PPC is caused by holes, not by electrons.

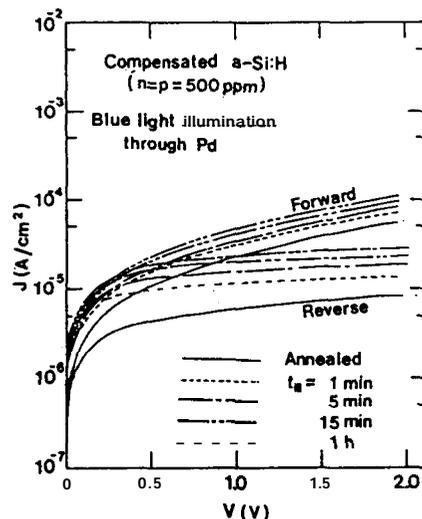


FIG. 6. Current-voltage characteristics of Schottky barrier structure after electron injection by illumination of blue light at 1 mW/cm^2 through the Schottky barrier side. [After Ref. 39]

The exposure time dependence of PPC and that of excess defect density in compensated SB structure are compared in Fig. 7. Defect density are obtained from the subband gap absorption by constant photocurrent method (CPM) subtracted by exponential absorption tail. The illumination was carried out with white light of 60 mW/cm^2 through IR absorbing filter. Up to 35 hour illumination, the magnitude of PPC and defect density increase in a very similar way. After resting 54 hours at room temperature and then annealing for 1 hour at 100°C , both PPC and defect density drop down by exactly the same ratio. This result indicate the close correlation between PPC effect and defect creation in compensated a-Si:H.

IV. DISCUSSION

In 1984, Hundhausen and Ley¹⁰ proposed AX center model in analogy with DX center of III-V compounds as being responsible to PPC in doping-modulated a-Si:H superlattices.

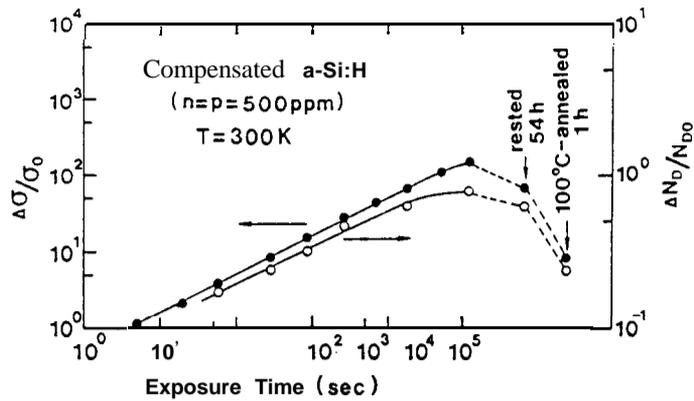


FIG. 7. Exposure-time dependence of PPC (●) and that of normalized excess defect density (○) in compensated Schottky barrier structure. σ_0 and N_{D0} are annealed values of dark conductivity and defect density, respectively. $\Delta\sigma$ and ΔN_D are excess conductivity and excess defect density, respectively. The resting of 54 hours and 100°C annealing for 1 hour were done after 35 hr. illumination. [After Ref. 39]

They assumed a strong electron-phonon coupling at AX center to form a thermal barriers for hole and electron trapping. Once a photoexcited hole is trapped at an AX center, it is no longer available for recombination with electrons, giving rise to PPC.

A similar model was proposed by Kakalios and Fritzsche¹⁴ and Kakalios²⁰ in which E-centers located in p-regions act as a similar hole center. This E-centers may trap a photoexcited hole or may release trapped electrons by photoexcitation during illumination accompanied by large lattice relaxations. Hole emission rate is small since the E-center underwent an atomic rearrangement, perhaps associated with the motion of a hydrogen or of a dangling bond. Thus trapped holes in E-centers, being in p-regions, are unable to recombine with electrons which are separated into n-regions.

From the similarities of PPC phenomena observed in compensated, unlayered a-Si:H films and in doping-modulated nnpnp ... a-Si:H superlattices, Argawal and Guha^{17,18,23} suggested either phosphorous-boron (P-B) complex or a boron complex in poor communication with outside as a special center responsible for PPC.

Su and Levine,^{19,21} on the other hand, claimed that dangling bonds are responsible for PPC in doping modulated superlattices. This claim was based on the fact that the magnitude of PPC depends strongly on the substrate temperature and the discharge gas composition in a similar manner as dangling bond density does. This model, however, fails to explain the existence of large PPC in fully compensated, unlayered film where least dangling bond density was observed.³⁴

In 1987, author's group²⁵ proposed a model in which the P-B-H complex as a hole trap in poor communication with outside act as the origin of PPC in both nnpnp ... doping-modulated superlattices and compensated, unlayered films. The model was based on the facts that PPC effect was permanently removed by relatively low temperature annealings: 300°C for doping modulated multilayers and 400°C for compensated films, that hydrogens tended to accumulate more at n-p interface regions on p-side³⁵ and that more P-B com-

plexes were calculated to exist near interface regions. We have also shown that PPC's in both doping-modulated superlattices and compensated, unlayered a-Si:H films are of the same origin.²⁸

Recently Kakalios^{36,37} proposed a model in which the Fermi energy shift away from valence band due to the reaction during illumination by



In other words, the captured hole converts an active boron dopant into inactive one, causing the rise of Fermi level toward the conduction band. In the case of doping-modulated superlattice, the reaction (1) proceeds in p-layers. The rise in Fermi level in p-layers pulls up the Fermi level toward conduction band in n-layers, giving rise to enhanced conductivity, i.e., PPC, since the conduction channel is the n-layer. In compensated samples rise in Fermi level directly gives rise to PPC. This model is a very convincing model since it does not require to assume any exotic trap centers.

On the other hand, Hamed and Fritzsche³⁸ proposed recently a different model in which PPC in doping-modulated superlattices is due to the dangling bond formation in p-layers during short period of illumination, forcing the Fermi level in p-layers to rise toward midgap and consequently pulling the Fermi level up in n-layers toward the conduction band, causing PPC.

Very recently, author's group³⁹ carried out hole and electron injection experiment by illuminating blue light into TCO side and into Schottky barrier side of TCO/n+/compensated a-Si:H/Pd structure. Only hole injection is found to cause PPC. From this, we concluded that hole-induced dopant conversion by one of following reactions



or



causes the rise of Fermi level toward conduction band, and consequently enhanced conductivity, PPC, in compensated films.

From all these models, we can draw conclusions that holes and dangling bonds have important bearing in PPC phenomena. In order to see definite roles of holes and dangling bonds, let us examine our recent experimental results on npnp ... doping modulated superlattices and compensated, unlayered films.

In the case of npnp ... doping-modulated a-Si:H superlattices, as we see in Fig. 1, PPC effect and dangling bond formation by illumination compete each other with PPC dominates at early stage and then dangling bond formation takes over. Fig. 2 tells us that dangling bonds can be formed in both n- and p-layers. Dangling bonds in p-layers anneal out more easily at lower temperatures while dangling bonds in n-layers are hard to anneal. Fig.

3. confirms that PPC prevails after short illumination, while dangling bonds are the dominant product by prolonged illumination.

Since holes are separated into p-regions and electrons into n-regions due to internal built-in modulation field, **p-regions** become hole rich while n-regions are electron rich. Since PPC effect and dangling bonds in p-layers anneal out at about the same temperature (By comparing Fig. 2 and Fig. 1 of Ref. 25), and since holes acts essential role in PPC effect, holes and dangling bonds have strong correlation in p-region. Thus reaction (2) and (3) can be good candidates for PPC.

Now consider an unlayered, compensated a-Si:H sample of SB structure. From the results shown in Figs. 4, 5 and 6, hole injection from TCO side enhance PPC while electron injection from SB side does not give any enhancement of PPC but defect formation in SB region. These results imply that holes, not electrons, cause PPC as in the case of doping-modulated superlattices.

On the other hand, the results of Fig. 7 tells us that PPC is always **accompanied** by dangling bond formation. The PPC and dangling bond density increase in exactly the same proportion with illumination time and anneal away in exactly the same proportion, again similar to the case of doping-modulated superlattices. In compensated samples, both P and B **dopants** exist in the same region. Thus we are led to the reaction (2) and (3) taking place in the compensated films.

In our previous **paper**,³⁹ we were not able to determine which of these two reactions take place in compensated **films**. From the close similarities of PPC and dangling bond formation and annealing behaviors between doping-modulated superlattices and compensated films, and also from the result of our earlier **result**²⁸ that PPC is the same origin both in the doping-modulated and compensated samples, we conclude that the reaction (3) is the predominant one as the origin of PPC. Namely, a hole is captured at four-fold coordinated boron (**B₄⁻**, active **dopant**) and neutral silicon with the result that a neutral three-fold coordinated boron (non-active) and a dangling bond (**Si₃[°]**) are created. Thus hole converts an active **accepter** and a neighboring silicon atom into a non-active boron impurity and a dangling bond. The reaction (2) can not proceed in doping-modulated superlattices because hole concentration is small in n-layers where phosphorous impurities are located. In the following we will present the most **comprehensine** model for PPC.

When a doping-modulated superlattice is illuminated by **-band-gap** light, electrons and holes are separated into n-and p-layers, respectively. Holes in p-layers are captured at four-fold coordinated boron (**B₄⁻**) acceptor and silicon network and then boron acceptors are converted into inactive 3-fold coordinated boron impurities (**B₃[°]**) and dangling bonds are created near the **midgap**. The conversion of **B₄⁻** into **B₃[°]** means the rise of Fermi level since the acceptor (**B₄⁻**) level was located near the valence band mobility edge in p-region, trying to pull the Fermi level toward it. Dangling bond formation also gives the effect of raising the Fermi level toward **midgap** from near the acceptor position in p-regions of doping-modulated superlattice. The rise of Fermi level in p-region changes the modulation in such a way that the Fermi level in n-region is also pulled up toward conduction band mobility edge since the Fermi level in n-region was forced to lower level by the Fermi level located near

valence band mobility edge in p-region. The rise of Fermi level in n-region means the increase in conductivity since conduction in doping-modulated superlattices is through n-layers. After prolonged illumination, dangling bonds are created very slowly in n-regions due to infrequent chances of the reaction (2) and e-h recombinations. This causes the PPC to drop down even below the annealed value as one can see in Fig. 1.

In the case of compensated sample, Fermi level lies near midgap before illumination due to the existence of both ionized donors (P_4^+) and acceptors (B_4^-). During illumination, electron-hole pairs are created. Some of the electron-hole pairs recombine to annihilate or to form dangling bonds, while some other electrons and holes are separated by diffusion possibly assisted by internal potential fluctuations caused by donor and acceptor impurities. Separated holes convert boron acceptor-silicon networks into inactive boron impurities and dangling bonds, causing the Fermi level to rise toward conduction band mobility edge with the additional pulling from active donors. The higher Fermi level means higher conductivity and consequently PPC. Since dangling bonds are formed near midgap, the rise of Fermi level is limited to a position somewhere between phosphorous donor P_4^+ and negative dangling bond (Si_3^-) positions. This is the reason why PPC in compensated unlayered samples show much smaller PPC than doping-modulated superlattices as seen in Fig. 8. In addition, charge separation effect in compensated sample is much less efficient due to the lack of large built-in field as in doping-modulated multilayers. As a result, the rate of increase in PPC is much slower in compensated film than in doping-modulated multilayers as seen in Fig. 8.

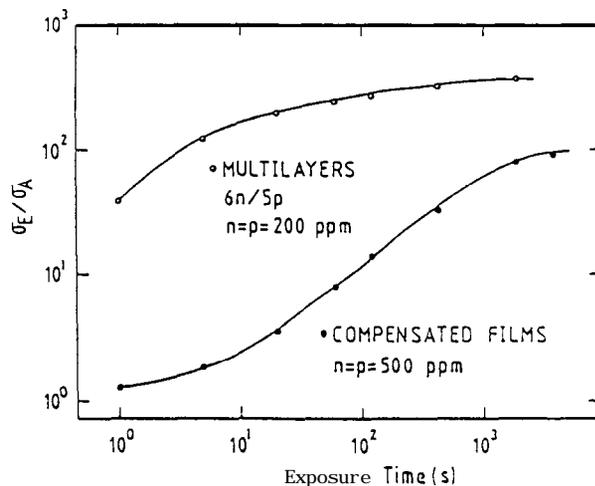


FIG. 8. Dependence of PPC (σ_E/σ_A) on exposure time for a doping-modulated superlattice (200 ppm each layer) and an unlayered, compensated sample (500 ppm each) at 300 K. σ_E is the conductivity measured at 4 min after the termination of illumination subtracted by the annealed state conductivity σ_A . The exposure light intensity was 50 mW/cm^2 . [After Ref. 25]

V. CONCLUSION

The most comprehensive model which can explain PPC in both doping-modulated superlattices and unlayered, compensated a-Si:H films is as follows: A hole-induced acceptor conversion into inactive one followed by a dangling bond formation is the origin of PPC in both doping-modulated superlattices and compensated films. The suppression of the rise of Fermi level by dangling bonds is the reason for smaller PPC in compensated films, while the rise of Fermi level in n-layers of doping-modulated superlattices is not suppressed because dangling bonds in n-layers are created only after prolonged illumination. PPC increase rate during illumination in compensated films is smaller because the chance of charge separation is smaller due to smaller built-in field than in doping-modulated superlattices.

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